

Mechanistic investigations of nanometer-scale lithography at liquid-covered graphite surfaces

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Pulse-induced nanometer-scale lithography has been performed on graphite surfaces that were in contact with pure water or other organic liquids. Very reproducible control over the pit diameter was observed in aqueous solutions, and a well-defined voltage threshold (4.0 ± 0.2 V) was also apparent. Near the threshold voltage, 7 \AA diameter $\times 2 \text{ \AA}$ high protrusions were formed, while larger initial pulse voltages resulted in pits of diameter $> 20 \text{ \AA}$.

Recently, atomic and molecular scale features have been produced on surfaces using scanning tunneling microscopy (STM) methods.¹⁻⁷ At room temperature, the smallest permanent lithographic process reported to date involves the formation of $\approx 40\text{-\AA}$ -diam, $\approx 3\text{-\AA}$ -deep pits on a highly ordered pyrolytic graphite (HOPG) surface.¹ These pits were formed by the application of 3–8 V pulses of 10–100 μs duration, while within tunneling distances. Although a substantial fraction of the STM tips successfully generated hundreds of uniform pits when subjected to constant amplitude and constant duration bias pulses,¹ the pulse threshold at which the smallest features were observed varied substantially from tip to tip. Additionally, the lithography process was observed to require a humid atmosphere and to exhibit daily fluctuations in pulse bias versus pit size. In order to elucidate the chemistry of this process, we have performed STM lithography studies of HOPG surfaces in contact with water and other organic liquids. For HOPG in $\text{H}_2\text{O}(l)$, we have observed a well-defined pulse threshold of $(4.0 \pm 0.2)\text{V}$, which reproducibly yielded 7-\AA -diam features that apparently protruded from the surface by 2 \AA . Larger voltage pulses yielded pits (with slightly larger dimensions) that were similar to those produced in air or in humid $\text{N}_2(g)$ atmospheres. This work demonstrates that subnanometer scale lithography can be accomplished on graphite at room temperature, and that STM studies can provide mechanistic information regarding the chemistry of the liquid-coated and gas phase lithographic processes.

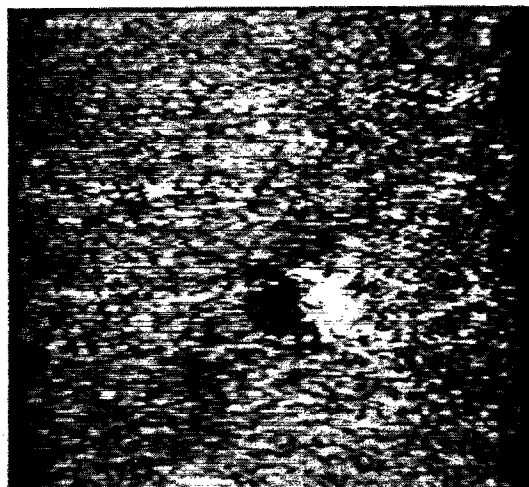
A STM specifically designed for imaging surfaces immersed in liquids was employed for this work.⁸ Bias pulses with a duration of 20 μs and an amplitude E_p of between -1 and -20 V (of the tip relative to the sample) were generated using a Wavetek model 802 pulse generator; most studies were performed with the tip negative relative to the sample in constant current mode, although qualitatively similar behavior was observed with the opposite tip polarity. The tip height versus position data (unfiltered) were displayed as images either in conventional constant

current fashion, or in a mode where the derivative of the tip height with respect to the X -scan direction was plotted versus position. No additional filtering, smoothing, or temporal averaging of the data was performed.

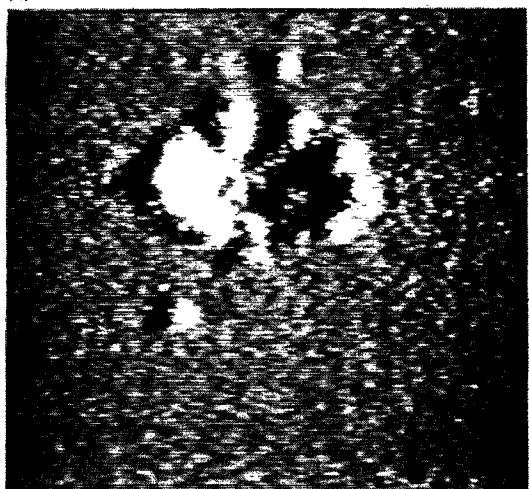
Electrochemically etched tungsten wires were used as the STM tips.⁸ After etching, the tips were insulated with poly(α -methylstyrene) (30 000 g/eq. MW, Aldrich) from a 30 w/vol % solution of the polymer in CH_2Cl_2 .⁹ In order to expose a small portion of metal tip for use in STM imaging under liquids, the polymer-coated tungsten tips were loaded into the STM and subjected to a "field emission" process at a bias of $+15 \text{ V}$ in air.⁹ Imaging experiments in pure $\text{N}_2(g)$ ambients were performed in a plexiglas glove box that had been thoroughly purged with dry $\text{N}_2(g)$. Rigorously dry toluene was obtained by distillation from CaH_2 in $\text{N}_2(g)$ followed by a second distillation, immediately prior to imaging, from $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$.

Figure 1 shows representative constant current STM data from HOPG in contact with $18 \text{ M}\Omega \text{ cm}$ resistivity $\text{H}_2\text{O}(l)$ after lithography had been performed. In the derivative mode images of Figs. 1(a) and 1(b), bright regions correspond to movement of the tip away from the surface, while dark regions indicate tip movement toward the surface. At higher derivative mode sensitivities, graphite atoms could be resolved in the background areas on such defect-free graphite regions before and after the lithographic feature was introduced; the sensitivity of the derivative mode image was reduced in the data of Fig. 1 to clearly illustrate the high contrast lithographic feature. Application of a 20 μs duration -4.0 V amplitude bias pulse while tunneling to the $\text{H}_2\text{O}(l)$ -covered graphite surface resulted in the derivative mode image of Fig. 1(a). As the tip traversed the feature in Fig. 1(a) from right to left, the signal generated was bright then dark, which is consistent with a protrusion in the surface topography. Cross sections of this feature revealed that it was 7 \AA in diameter and $\sim 2 \text{ \AA}$ in height [Fig. 1(c)]. Domed features like that shown in Fig. 1(a) could be generated using $> 90\%$ of the tips employed for lithography in $\text{H}_2\text{O}(l)$ with $E_p = \pm(3.8\text{--}4.2\text{V})$. These "domed" features (i.e., features that caused the tip to traverse a domed-shape profile due to increases in either the surface height or in the tunneling

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(a)



(b)

probability) were stable to imaging at biases as high as ± 500 mV for periods of > 1 h under the $\text{H}_2\text{O}(l)$ ambient.

The features in Fig. 1(a) were only formed on graphite surfaces that were in contact with liquid H_2O , and only with pulses near the observed threshold voltage. Incrementally larger bias pulse amplitudes of $E_p = \pm(4.3 - 4.4)$ V produced pits that were qualitatively identical to those observed for lithography on HOPG in air;^{1,2} the diameter of a typical pit formed with a -4.2 V pulse under $\text{H}_2\text{O}(l)$ was 40 Å, and its depth was 3 Å. This depth is consistent with the removal of a single graphite layer, as proposed earlier for bias-pulse lithography on HOPG in gaseous ambients.^{1,2} Further increases in the bias pulse amplitude resulted in monotonic increases in the dimensions of the resulting pit. As a representative example, Fig. 1(b) shows a derivative mode STM image of an 80 -Å-diam pit that was generated with a tip bias pulse amplitude of -4.5 V for HOPG in contact with $\text{H}_2\text{O}(l)$. Note that the darker region now appears first in the right-to-left scan direction of Fig. 1(b), which is the expected signal for a depression in the surface.

The reproducibility of bias-pulse lithography in $\text{H}_2\text{O}(l)$ improved in two distinct ways relative to the process in an air ambient. The reproducibility of the threshold voltage (i.e., the voltage required to produce the smallest

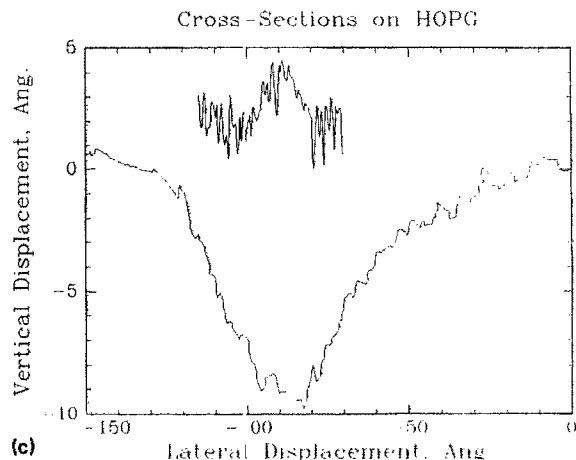


FIG. 1. STM images of lithographically modified HOPG in pure water. All images show derivative mode data obtained at a bias of -100 mV, a fast raster frequency (x direction) of 10 Hz, and a slow raster frequency (y direction) of 0.025 Hz. (a) Domed feature produced at HOPG in pure water using a -4.0 V $\times 10$ μs bias pulse. Image window is 80×80 Å. (b) Large pit (diameter ≈ 80 Å) produced at HOPG in pure water using a -4.5 V $\times 20$ μs pulse. Image window is 400×400 Å. (c) Cross sections of the features in (a) and (b) above. The smaller scan line with the positive vertical displacement corresponds to the feature of (a); the other trace refers to the feature depicted in (b).

observed features) was observed to be (-4.0 ± 0.2) V in $\text{H}_2\text{O}(l)$ for a large number of independent experiments with a variety of STM tips. In contrast, experiments in laboratory air exhibited substantial daily variations of as much as 5 V in the pulse threshold, presumably due to variations in the relative humidity.¹⁰ Second, in $\text{H}_2\text{O}(l)$ the relationship between E_p and the pit (or dome) diameter was very well defined for pulse amplitudes above E_p . Fig-

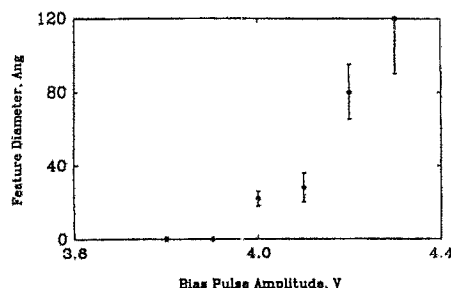


FIG. 2. Statistics for the feature diameter as a function of the bias pulse amplitude for lithography experiments at HOPG in water. Each data point represents 10 trials conducted with several polymer-coated tungsten tips over a seven day interval. Error bars are the calculated 1σ confidence interval for these data. Two additional points not displayed are as follows: $V = 4.40$ V, diameter = 210 ± 85 Å; $V = 4.60$ V; diameter = 505 ± 155 Å.

ure 2 shows statistics relating E_p to the feature diameter; these statistics were obtained using 10 polymer-coated tungsten tips that were fabricated and used in STM lithography experiments over the period of a week. The increased reproducibility obtained in $\text{H}_2\text{O}(l)$ underscores the link between the chemistry of the lithography process and the presence of water during the pulse period.

Several different ambients were investigated in order to confirm the suggestion that H_2O is required to form etch pits. At graphite surfaces in contact with either dry toluene(l) or dry $\text{N}_2(g)$, features could not be generated even with pulse amplitudes as large as ± 10 V. However, introduction of H_2O into either of these ambients restored the ability to produce the features represented in Figs. 1(a) and 1(b). These observations are consistent with those of Terashima *et al.*² who observed a suppression of pit formation on graphite in 10 mTorr toluene vapor and in dry $\text{N}_2(g)$ ambients. Reagent grade organic solvents which were not rigorously dried, such as *n*-octane and mineral oil, behaved qualitatively like an air ambient. In these impure liquids, variations of the threshold voltage of up to several volts were observed, but in all cases lithography was facilitated at $|E_p| < 10$ V. In these ambients, the lithography operation yielded only pits, as was observed for experiments in air ambient.

For graphite surfaces in contact with $\text{H}_2\text{O}(l)$, the observation of small diameter "domes" at the voltage pulse threshold suggests that these features are intermediates in the formation of the pits that are observed at larger voltages in $\text{H}_2\text{O}(l)$ and at all voltages larger than the threshold voltage in humid air. This hypothesis was supported by the observation that in contact with $\text{H}_2\text{O}(l)$, domes could be converted into 30–40 Å diameter pits by application of a subthreshold, 0.2 V pulse. This indicates that the domes are metastable intermediates, and that they can be converted into pits with suitable physical or chemical stimuli. This also suggests that chemical reagents might be able to recognize these lithographically produced metastable reactive sites and could yield specific reactions at predetermined positions on the HOPG surface.

Although the chemical structure of the "dome" has not been identified in this work, one possibility consistent with the available data is apparent from an energy minimized structure of a 15 carbon molecular analog of the graphite surface, in which one 6 carbon ring has been transformed from sp^2 (trigonal carbon) to sp^3 (tetrahedral carbon) hybridization.¹¹ This calculation indicated that the sp^3 carbons puckered out of the graphite surface, producing a domed structure which had dimensions of 7 Å (diameter) and 0.45 Å (height). These dimensions are consistent with the observed feature size in Fig. 1(a). The rehybridization also produced a significant increase in the calculated bond angles for both these sp^3 carbons, and for the sp^2 carbons to which they are bonded. If this model is correct, it also predicts that the domed features will exhibit enhanced reactivity relative to the pristine graphite surface, and such reactivity was observed experimentally in the ability to convert the domes to pits with a subthreshold voltage pulse. While the exact mechanism responsible for

the formation of the lithographic structures like that shown in Fig. 1 cannot be identified from the available data, an electrochemical mechanism seems unlikely in view of the observed polarity independence of the lithography process. Although the strain-induced structure represents one plausible candidate for a defect structure, Mizes and coworkers^{12,13} and Soto¹⁴ have predicted that a variety of defect types are capable of inducing an increase in the local density of states on graphite surfaces and thus yield a local increase in the tunneling probability; clearly, alternative mechanisms can only be definitively ruled out when the chemical structures of the "dome" and "pit" features are available.

In conclusion, we have shown that STM-based lithography of HOPG in contact with $\text{H}_2\text{O}(l)$ is reproducible, leads to subnanometer diameter features not observed previously in gaseous ambients, and leads to improved control over pit diameter at larger voltage pulses. Attempts to exploit these reactive features to achieve site-specific, nanometer-scale chemical derivatization of surfaces is under study at present.

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